

# Jarzynski Equality and Irreversibility

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## Abstract

Using methods of phenomenological non-equilibrium thermodynamics, the proof is performed that Jarzynski's equality is only valid in the reversible limit and that a conclusion to non-equilibrium inequalities concerning free energy and work is not possible and therefore not allowed.

## 1 Introduction

In 1997, C.Jarzynski considered a system coupled to a heat reservoir [1]. The time development of this isolated compound system in its phase space was governed by a 3-term Hamiltonian. That part of the Hamiltonian which belonged to the system itself, included a work variable which could be “switched”, that means, power could be exchanged between the system and its environment, the heat reservoir. Starting out from an equilibrium state in the phase space, represented by a canonical ensemble, the system was carried on by “switching” along an isothermal trajectory into an equilibrium final state. There were different possibilities of “switching” generating different trajectories between the initial and final equilibrium states forming an ensemble over which could be averaged. The free energy difference between the fixed initial and final states was identical for all trajectories of the ensemble, whereas the the work, the integrated power along the trajectory, was different depending on the manner of “switching”. Because of using a canonical ensemble, Jarzynski obtained an equilibrium equality connecting the free energy difference to the averaged work, and he was of the opinion, that from this equality non-equilibrium inequalities can be derived establishing a microscopic Hamiltonian basis for the increase of entropy. This supposition is rejected in this paper.

Because in Statistical Physics often assumptions are necessarily made – such as the interaction energy must be small, Liouville's theorem is still valid in non-equilibrium, the canonical system temperature is close to the thermostatic temperature of the controlling reservoir, the time rate of the work variables is infinitely slow– which are difficult to judge from a non-equilibrium thermodynamical view, it would be

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useful to look for a common basis of both disciplines. Here, we start out with non-equilibrium state spaces and the non-equilibrium entropy defined on them. The non-equilibrium contact temperature is used for defining the free energy and its time rate. For approaching Jarzynski, the difference of the time rate of the free energy and the power is derived for different non-equilibrium processes between two equilibrium states, the initial and the final ones. An inequality generalizing Jarzynski's equality to non-equilibrium is derived and Jarzynski's equality is discussed from the view of non-equilibrium thermodynamics. Jarzynski's supposition that from equilibrium can be concluded to non-equilibrium is falsified concerning the considered equality.

## 2 Sketch of Non-Equilibrium Thermodynamics

### 2.1 Phenomenological basic variables

If we consider a discrete thermodynamical system, its state is described by basic variables. Kind and number of these variables depend on the nature of the system under consideration and on the process going on in the system. The number of variables in non-equilibrium is clearly greater than that in equilibrium. Therefore, equilibrium needs a minimal number of basic variables spanning the so-called equilibrium sub-space. According to a special formulation of the Zeroth Law [2], it is spanned for a thermally homogeneous<sup>1</sup> system by

$$\mathbf{z}_{eq} = (U, \mathbf{a}, \mathbf{n}) \quad \text{or} \quad \mathbf{z}_{eq} = (T, \mathbf{a}, \mathbf{n}) \quad (1)$$

(internal energy  $U$ , work variables  $\mathbf{a}$ , mole numbers  $\mathbf{n}$ , thermostatic temperature  $T$ ). There exists an one-to-one mapping between the internal energy and the thermostatic temperature  $U \leftrightarrow T$  in equilibrium.

More basic variables than the equilibrium ones are needed in non-equilibrium

$$\mathbf{z} = (U, \mathbf{a}, \mathbf{n}, \mathbf{z}_{neq}). \quad (2)$$

The set of the non-equilibrium variables depend on the nature of the system in consideration: e.g. the orientation of needle-shaped molecules may be an example in the case of complex materials, time derivatives of the equilibrium variables an other one. Be as it may, two kinds of basic non-equilibrium variables are necessary for each non-equilibrium system: variables  $\boldsymbol{\xi}$  which generate the entropy production [3]

$$\Sigma = \boldsymbol{\beta} \cdot \dot{\boldsymbol{\xi}} \geq 0, \quad (3)$$

and a non-equilibrium temperature  $\Theta$  which is independent of the internal energy and which is discussed in the next section. The inequality (3) represents the Second Law of Thermodynamics [4].

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<sup>1</sup>A system without any adiabatic partitions

## 2.2 Non-equilibrium temperature

We start out with the defining inequality of the contact temperature  $\Theta$  [5, 6, 7]

$$\dot{Q} \left( \frac{1}{\Theta} - \frac{1}{T^*} \right) \geq 0. \quad (4)$$

Here,  $\dot{Q}$  is the net heat exchange between the considered discrete system and its equilibrium environment of the thermostatic temperature  $T^*$ . According to this defining inequality, we have the following

*Definition of the contact temperature:*  $\Theta$  is that thermostatic temperature of the equilibrium environment for which the net heat exchange between the system and this environment through an inert partition vanishes [8].

From (4), the following inequalities follow directly which express the definition of the contact temperature analytically:

$$T^* > \Theta \iff \dot{Q} > 0, \quad T^* < \Theta \iff \dot{Q} < 0. \quad (5)$$

This inequalities make possible to measure the contact temperature by calorimetry.

The thermal contact between system and environment cannot be described by its thermostatic temperature related to the internal energy in non-equilibrium. Consequently, we need a non-equilibrium temperature which is independent of the internal energy and which is determined by the zero of the net heat exchange between system and environment<sup>2</sup>.

## 2.3 Non-equilibrium entropy, First Law and free energy

The time rate of the non-equilibrium entropy is an analogue to Gibbs fundamental equation defined on the basic non-equilibrium variables (2) [9]

$$\dot{S} := \frac{1}{\Theta} \dot{U} - \frac{\mathbf{A}}{\Theta} \cdot \dot{\mathbf{a}} - \frac{\boldsymbol{\mu}}{\Theta} \cdot \dot{\mathbf{n}} + \alpha \dot{\Theta} + \beta \cdot \dot{\boldsymbol{\xi}}. \quad (6)$$

According to (6), the basic variables (2) are

$$\mathbf{z} = (U, \mathbf{a}, \mathbf{n}, \Theta, \boldsymbol{\xi}). \quad (7)$$

Introducing the molar enthalpy  $\mathbf{h}$  and the external change of mole numbers  $\dot{\mathbf{n}}^e$  by the material exchange between system and environment [10], the First Law and the power  $\dot{W}$  are

$$\dot{U} = \dot{Q} + \dot{W} + \mathbf{h} \cdot \dot{\mathbf{n}}^e, \quad \dot{W} := \mathbf{A} \cdot \dot{\mathbf{a}}. \quad (8)$$

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<sup>2</sup>The contact temperature is here only introduced by a sketch. More details can be found in [6, 9]

Approaching Jarzynski's equality, we consider closed discrete systems without chemical reactions

$$\dot{\mathbf{n}} \doteq \mathbf{0} \quad \dot{\mathbf{n}}^e \doteq \mathbf{0}. \quad (9)$$

As announced, we now derive the

□**Proposition:** Internal energy and contact temperature are independent variables.

Along a non-equilibrium process, the contact temperature is generally a function of time  $\Theta(t)$ . If a closed system without power exchange, is contacted along this process with a family of heat reservoirs whose thermostatic temperatures  $T^*(t)$  at the contact time  $t$  are of the special choice

$$T^*(t) \doteq \Theta(t) \wedge \dot{W} = 0 \implies \dot{Q}(t) = 0, \quad (10)$$

the net heat exchange vanishes, and we obtain from (8) and (10)

$$\dot{U}(t) = 0 \quad \text{and} \quad \Theta(t) \neq 0, \quad (11)$$

demonstrating the independence of  $\Theta$  and  $U$ . □

The (non-equilibrium) free energy is defined by

$$F(\mathbf{a}, \Theta, \xi) := U - \Theta S \implies \dot{F} = \dot{U} - (\Theta S)^\bullet, \quad (12)$$

resulting in

$$\dot{F} = \dot{Q} + \dot{W} - (\Theta S)^\bullet \implies \dot{F} - \dot{W} = -(S + \alpha\Theta) \dot{\Theta} - \Theta\Sigma \quad (13)$$

by taking (8) and (6) into account. For an isothermal process<sup>3</sup>, we obtain the dissipated power

$$\dot{\Theta} \doteq 0 \implies \dot{F} - \dot{W} = -\Theta\Sigma \leq 0. \quad (14)$$

If the entropy of the equilibrium environment –that is the controlling heat reservoir– is denoted by  $S^*$  and its thermostatic temperature by  $T^*$ , the net heat exchange between system and environment can be represented by [11]

$$\dot{Q} = -T^* \dot{S}^*. \quad (15)$$

Inserting this into (13)<sub>1</sub>, we obtain the thermodynamical starting point of Jarzynski's considerations

$$\dot{F} - \dot{W} = -T^* \dot{S}^* - (\Theta S)^\bullet \quad (16)$$

with the essential difference that in [1] the contact temperature is replaced by the thermostatic temperature  $T = 1/k\beta$  of the system also in non-equilibrium.

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<sup>3</sup>how to perform such a process is discussed below

This thermostatic temperature is as in equilibrium related to the internal energy, so that this replacement cancels one non-equilibrium variable.

$$\Theta \doteq T \implies \dot{F} - \dot{W} = -T^* \dot{S}^* - (TS)^{\bullet}. \quad (17)$$

From (14) follows

$$\dot{\Theta} \doteq \dot{T} \doteq 0 \implies \dot{F} - \dot{W} = -T\Sigma \leq 0. \quad (18)$$

### 3 The Processes

Jarzynski considers a set of non-equilibrium processes in the phase space of a closed system [1]. All processes of this family starting from an equilibrium state  $A^{eq}$  and ending in an other equilibrium state  $B^{eq}$  are controlled by a heat reservoir of the thermostatic temperature  $T^*$ . The time rates of the processes are generated by a Hamiltonian which also includes the interaction energy between the system and the heat reservoir representing the equilibrium environment. Along each process of that family, the system exchanges power  $\dot{W}$  and heat  $\dot{Q}$  with its environment.

Whereas in phenomenological non-equilibrium thermodynamics the family of the non-equilibrium processes between  $A^{eq}$  and  $B^{eq}$  is arbitrary, Jarzynski chooses processes in the phase space which are distributed according to a canonical ensemble<sup>4</sup> with the same constant temperature as that of the controlling heat reservoir:  $T = T^* = 1/k\beta$ . That is really a restricting presupposition, because

- i): a thermostatic temperature is not an adequate variable of a non-equilibrium system<sup>5</sup>,
- ii): if system and controlling heat reservoir have the same (thermostatic) temperature, the heat exchange between them vanishes<sup>6</sup>.

This is just the aim of this paper: to elucidate Jarzynski's procedure by methods of phenomenological non-equilibrium thermodynamics.

#### 3.1 Dissipated work

There is a lot of different formulations of the Second Law [4, 12]: in field formulation of thermodynamics [7] and for discrete systems as (3) or the Sears-Kestin statement [13]. Similiar formulations stem from (13) and (16) by integrating along processes  $\mathcal{C}_k : A^{eq} \rightarrow B^{eq}, k = 1, 2, 3, \dots$ , which all run between the

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<sup>4</sup>that means, he presupposes that the system is in equilibrium, what only fits to the presupposed non-equilibrium processes in the phase space, if those are interpreted as entropy generating fluctuation processes around equilibrium.

<sup>5</sup>Jarzynski does not consider a general non-equilibrium system, but a thermal fluctuating equilibrium system.

<sup>6</sup>the usual evasion in thermostatic runs as follows: There is a reversible heat exchange  $\rightarrow$  a topic which does not exist

equilibrium states  $A^{eq}$  and  $B^{eq}$  and which are controlled by an equilibrium environment of the temperature  $T^*$

$$\begin{aligned} \mathcal{C}_k \int_{Aeq}^{Beq} \dot{F} dt - \mathcal{C}_k \int_{Aeq}^{Beq} \dot{W} dt &= \\ &= -\mathcal{C}_k \int_{Aeq}^{Beq} (S + \alpha\Theta) \dot{\Theta} dt - \mathcal{C}_k \int_{Aeq}^{Beq} \Theta \Sigma dt = \end{aligned} \quad (19)$$

$$= -\mathcal{C}_k \int_{Aeq}^{Beq} T^* \dot{S}^* dt - \mathcal{C}_k \int_{Aeq}^{Beq} (\Theta S)^\bullet dt. \quad (20)$$

The left-hand side of (19)/(20) is the dissipated work along processes  $\mathcal{C}_k$  belonging to a process family between two fixed equilibrium states,  $A^{eq}$  and  $B^{eq}$ , of the system which is controlled by an equilibrium environment marked by  $*$ . Both expressions (19)/(20) are derived by methods of non-equilibrium thermodynamics. They differ: (19) contains the time rate of the contact temperature which does not appear in (20). The processes considered by Jarzynski in the phase space of the system have their thermodynamical analogue in the process family  $\{\mathcal{C}_k\}$ .

The path integrals along  $\mathcal{C}_k$

$$\mathcal{C}_k \int_{Aeq}^{Beq} \dot{F} dt =: \Delta F, \quad (21)$$

$$\mathcal{C}_k \int_{Aeq}^{Beq} (\Theta S)^\bullet dt = (\Theta S)_{Beq} - (\Theta S)_{Aeq} = T^*(S_{Beq} - S_{Aeq}) \quad (22)$$

are path-independent. If the temperature of the environment is time independent, (20) becomes

$$T^* = \text{const} : \quad \Delta F - W_k = -T^*(S_{Beq}^* - S_{Aeq}^*) - T^*(S_{Beq} - S_{Aeq}), \quad (23)$$

$$W_k := \mathcal{C}_k \int_{Aeq}^{Beq} \dot{W} dt. \quad (24)$$

Presupposing that the compound system consisting of the system itself and its environment is an isolated one, we obtain by the Second Law in the case of additive entropies

$$(S^* + S)^\bullet \geq 0 \implies S_{Beq}^* - S_{Aeq}^* + S_{Beq} - S_{Aeq} \geq 0 \quad (25)$$

resulting in

$$T^* = \text{const} : \quad \Delta F - W_k \leq 0, \quad \wedge k, \quad (26)$$

the well known statement, that for irreversible isothermal<sup>7</sup> processes the minimum of dissipated work is given by the difference of the corresponding free energy in the case of reversibility<sup>8</sup>

$$\text{reversible} \wedge T^* = \text{const} : \quad \Delta F - W_k = 0, \quad \wedge k. \quad (27)$$

How to obtain Jarzynski's equality is discussed in the next section.

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<sup>7</sup>attention: the environment is isothermal, but the contact temperature of the system is time dependent

<sup>8</sup>reversible "processes" do exist in nature

### 3.2 The ensemble average

We now consider two realisations of the process family  $\{\mathcal{C}_k\}$  between the equilibrium states  $A^{eq}$  and  $A^{eq}$ : the non-equilibrium processes on the state space (7) and the trajectories in the phase space of the system. Both kinds of processes form an ensemble which obeys (26). According to Jarzynski, we introduce an ensemble average by

$$\overline{W} := \frac{1}{N} \sum_{k=1}^N W_k \quad \Longrightarrow \quad T^* = \text{const} : \quad \Delta F - \overline{W} \leq 0, \quad (28)$$

and we obtain the current inequality #1) in [1]. Adapting (28) to the canonical ensemble used by Jarzynski, we introduce its temperature parameter  $\beta$  and obtain the inequalities

$$T^* = \frac{1}{k\beta} = \text{const} : \quad \exp(-\beta\Delta F) \geq \exp(-\beta W_k) \quad (29)$$

$$\Longrightarrow \quad \exp(-\beta\Delta F) \geq \frac{1}{N} \sum_{k=1}^N \exp(-\beta W_k) =: \overline{\exp(-\beta W)}. \quad (30)$$

Against expectation, we end up with the inequality (30) which is not discovered by Jarzynski's procedure. The question –what about the equation ?– is easy to answer: It is valid in the reversible case (27)

$$\text{reversible} \wedge T^* = \text{const} : \quad \exp(-\beta\Delta F) = \overline{\exp(-\beta W)}. \quad (31)$$

Consequently, the validity of Jarzynski's equality from a thermodynamical point of view is clear: It is only valid in the reversible limit.

## 4 Ex- and in-isothermal processes

The derivation of Jarzynski's equality (31) launches with (20) by contacting the system with a heat reservoir of constant temperature  $T^*$ . Along this process, the contact temperature  $\Theta$  is not constant in general. Consequently, we have to distinguish between two different isothermal processes distinguished by different names

$$T^* = \text{const} \quad \Longrightarrow \quad \text{ex-isothermal}, \quad (32)$$

$$\Theta = \text{const} \quad \Longrightarrow \quad \text{in-isothermal}. \quad (33)$$

The question arises, how to perform an in-isothermal process: the system has to be controlled by a family of in time changing heat reservoirs of thermostatic temperatures  $T^*(t)$ , so that during the process  $\Theta(t) = \text{const}$  is enforced. Starting out with the defining inequality (4), the heat exchange can be represented by a constitutive equation

$$\dot{Q} = \kappa[T^* - \Theta], \quad \kappa = f(T^* - \Theta) \geq 0, \quad f' \neq 0. \quad (34)$$

Time differentiation results in

$$\partial_t \dot{Q} = \left( f'[T^* - \Theta] + f \right) [\dot{T}^* - \dot{\Theta}]. \quad (35)$$

For in-isothermal processes, we obtain

$$\dot{\Theta} \doteq 0 : \quad \dot{T}^*(\partial_t \dot{Q}, T^* - \Theta) \equiv \dot{T}^*(t) = \frac{\partial_t \dot{Q}}{f'[T^* - \Theta] + f} \quad (36)$$

the time rate of the thermostatic temperatures  $T^*(t)$  of the family of heat reservoirs enforcing the in-isothermal process.

For an in-isothermal process, (19) becomes analogously to (26)

$$\Delta F - W_k^{inis} = -\Theta \mathcal{C}_k^{inis} \int_{Aeq}^{Beq} \Sigma dt \leq 0. \quad (37)$$

An ensemble average analogously to (28) is also possible

$$\Theta = \text{const}: \quad \Delta F - \overline{W^{inis}} \leq 0. \quad (38)$$

In the reversible case

$$T^* = \Theta = \frac{1}{kT} = \text{const} \implies \Delta F - \overline{W^{inis}} = 0 \quad (39)$$

we rediscover Jarzynski's equality.

## 5 Discussion

Jarzynski's argumentation in [1]

“ the inequality  $\overline{W} \geq \Delta F$  follows directly from the equality  $\exp(-\beta \overline{W}) = \exp(-\beta \Delta F)$  by application of the mathematical identity  $\overline{\exp x} \geq \exp \overline{x}$ <sup>9</sup>. This establishes  $\overline{W} \geq \Delta F$  directly from a microscopic Hamiltonian basis rather than by invoking the increase of entropy”

is not true: for deriving Jarzynski's equality, reversibility must be presupposed: Irreversibility cannot be replaced by application of a mathematical identity. Consequently, the following scheme is valid

$$\text{irreversible} \implies \Delta F \leq \overline{W} \implies \exp(-\beta \Delta F) \geq \overline{\exp(-\beta W)} \quad (40)$$

$$\Delta F = \overline{W} \iff \exp(-\beta \Delta F) = \overline{\exp(-\beta W)} \iff \text{reversible} \quad (41)$$

Presupposing reversibility and therefore Jarzynski's equality, application of Jensen's inequality is of course allowed, but only the equation is valid because of physical reasons. Also clear is, that by presupposing a canonical ensemble, reversibility follows necessarily.

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<sup>9</sup>Jensen inequality



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